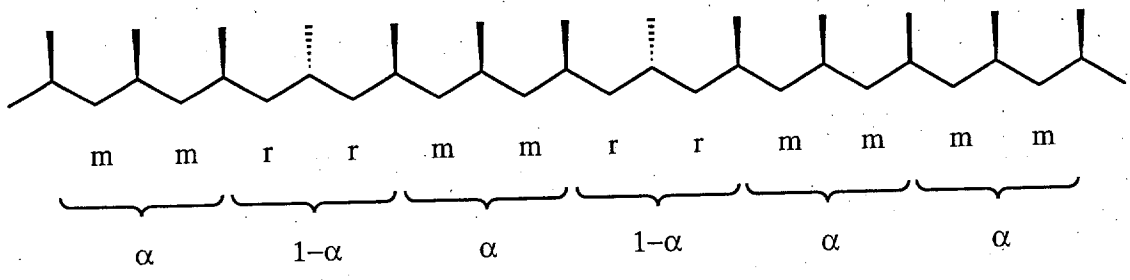
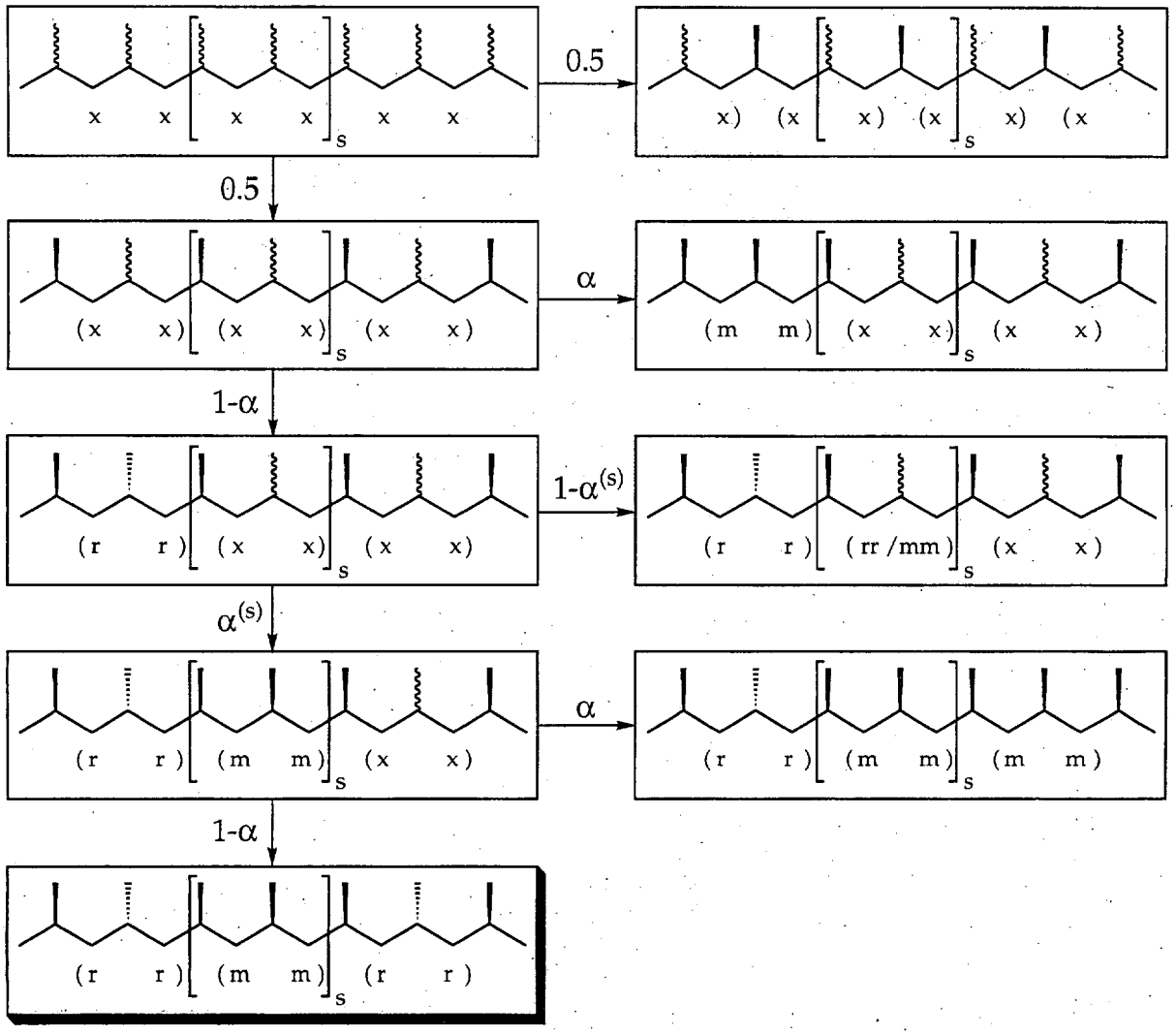
Derivation of the Isotactic Block Length Distribution for Isotactic-hemiisotactic Polypropylene. For a hemiisotactic regime, every other stereocenter is of the same stereochemistry and the intervening stereocenters are of variable stereochemistry. Therefore, as in the hemiisotactic polymer shown below, a given polymer can be represented by a string of mm and rr triads. This disallows the pentads containing isolated m and r dyads: mmrm, rrmr and mrmr. For a given triad, if the probability of obtaining an mm triad is defined as α, then the probability of obtaining an rr triad is 1-α.



An isotactic block is defined as a collection of m dyads terminated on either end by an r dyad. Since only sequential mm and rr triads are allowed for hemiisotactic polypropylene, an isotactic block must be a collection of mm triads terminated on either end by an rr triad: (rr)(mm)$^{(s)}$(rr), where s is the number of repeating mm triads. The probability of finding such a sequence is determined as follows.

In a hemiisotactic polymer, half of the monomers are at the start of an allowed triad and half of the monomers reside in the middle of an allowed triad. Therefore, the probability that a randomly selected monomer *begins* a sequence of allowed triads is 0.5. The probability that the first triad is rr is given by 1-α. The probability of then finding a sequence of mm triads is given by $\alpha^{(s)}$, where s is the number of repeating triads. Finally the probability of terminating the isotactic sequence with an rr triad is 1-α. Since

the variables s and n are related as s = ((n-1)/2), we can generalize for the probability of obtaining an isotactic block containing n repeating monomer units: P_n = $(0.5)(1-\alpha)(\alpha)^{((n-1)/2)}(1-\alpha)$, for n = odd.



A special situation arises for n=1. In addition to $(0.5)(1-\alpha)(\alpha)^{(0)}(1-\alpha) = (0.5)(1-\alpha)^2$, an isotactic block of length 1 occurs with the central monomer of *every* rr triad. The probability of this occurrence is $(0.5)(1-\alpha)$ because half of all monomers insert at the center of an allowed triad and $1-\alpha$ of these insert to provide the rr triad. Therefore, P_1 = $(0.5)(1-\alpha)^2 + (0.5)(1-\alpha)$.

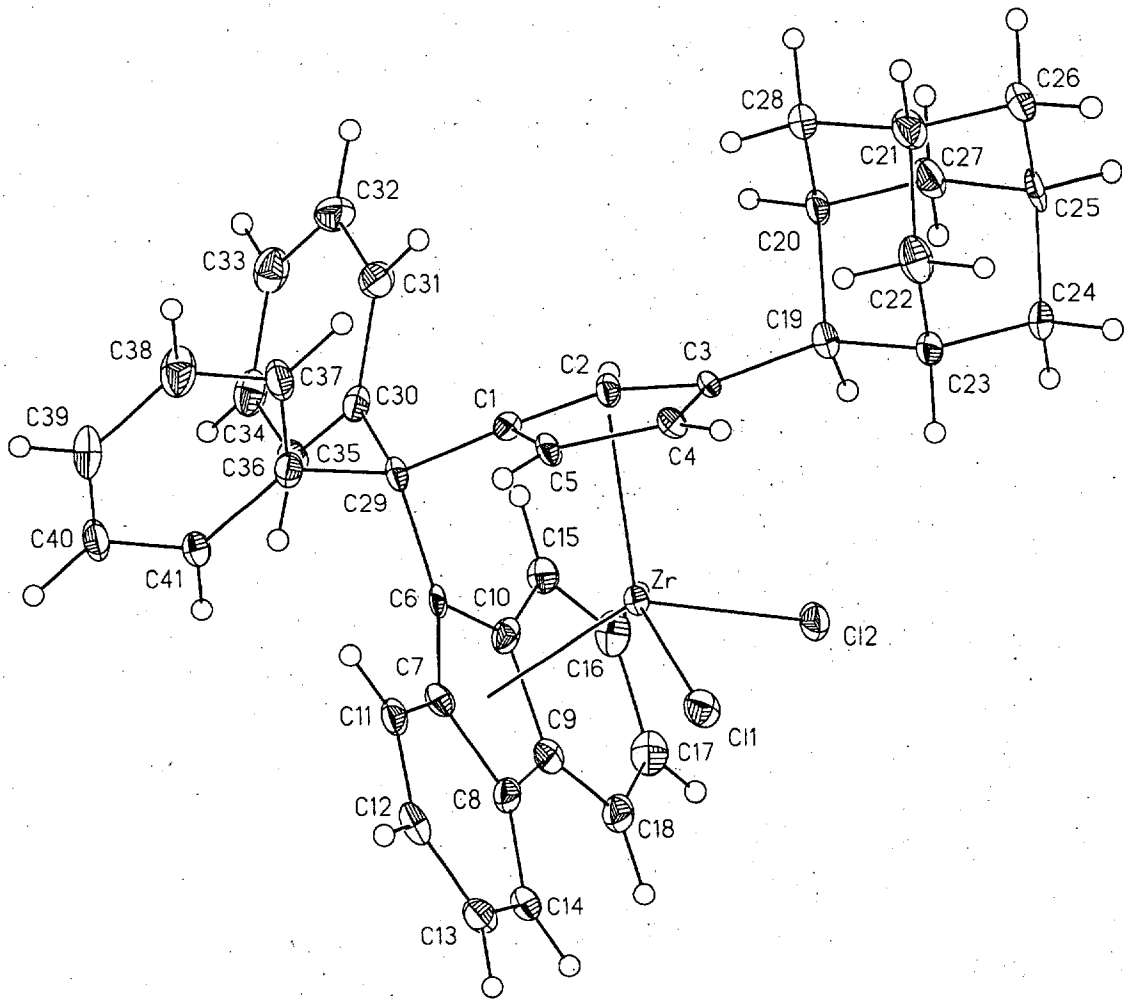
For a given polymer chain, the number of blocks of length n present is given by $N_n = P_n$ (DP), where DP is the degree of polymerization—the number of monomers in that chain—which equals the number average molecular weight/monomer molecular weight (= $M_n/42.08$ for polypropylene).[25]

4

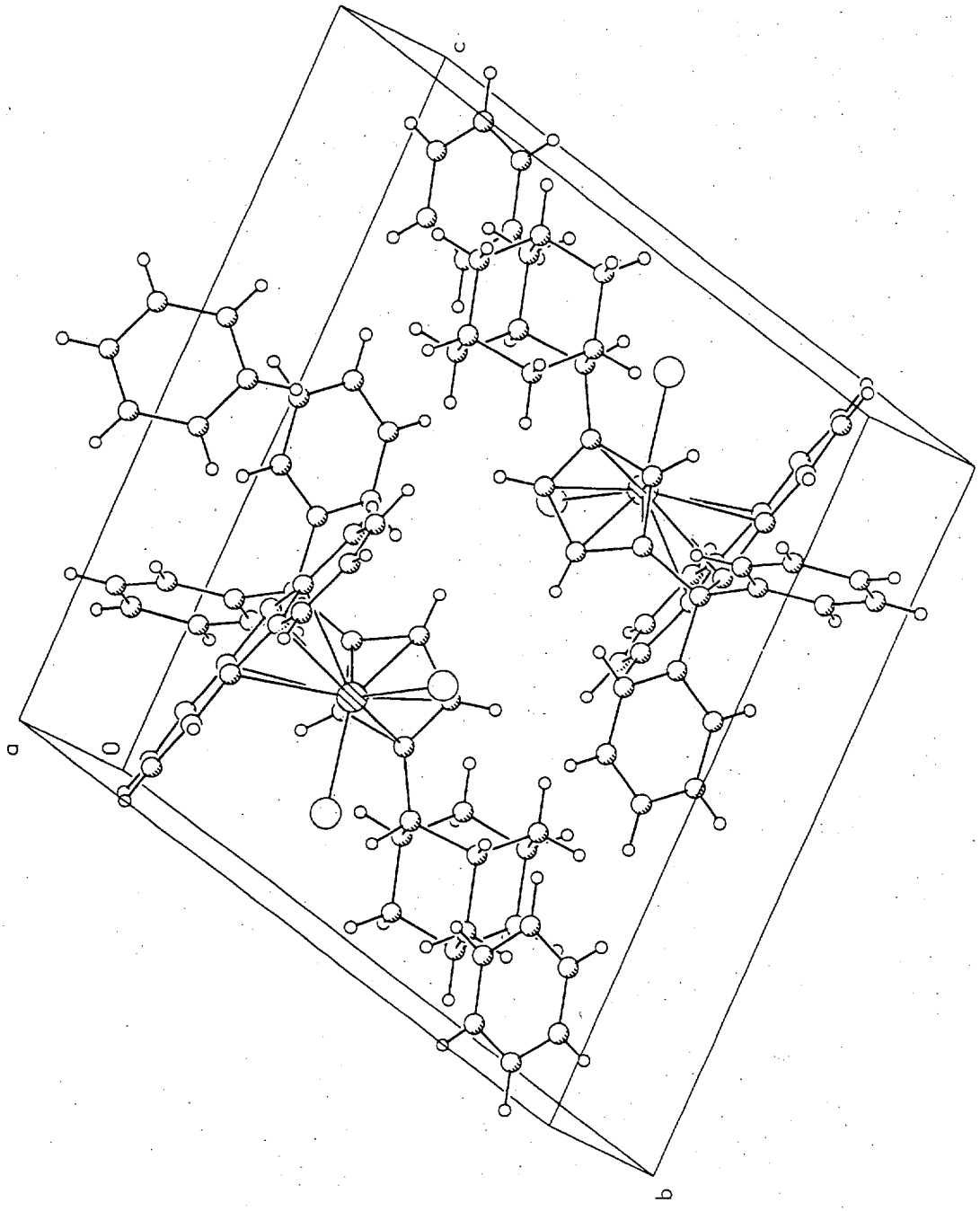
X-ray Crystal Structure Data for

$Ph_2C(C_{13}H_8)(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2 \cdot (C_6H_6)_{1.5}$

Cambridge Database (CCDC) 137247



Labeled view with 50% probability ellipsoids



Depiction of unit cell contents showing the unit cell boundaries

Table 1. Crystal data and structure refinement for $Ph_2C(C_{13}H_8)(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2$.

Empirical formula	$C_{50}\ H_{45}\ Cl_2\ Zr\ (C_6H_6)_{1.5}$	
Formula weight	808.03	
Crystallization solvent	benzene	
Crystal habit	thick blade	
Crystal size	0.42 x 0.41 x 0.08 mm^3	
Crystal color	red	
Data Collection		
Type of diffractometer	CCD area detector	
Wavelength	0.71073 Å MoKa	
Data collection temperature	98(2) K	
Theta range for 5068 reflections used in lattice determination	2.57 to 28.16°	
Unit cell dimensions	a = 9.4262(18) Å	a= 103.984(3)°
	b = 13.514(3) Å	b= 90.944(3)°
	c = 15.357(3) Å	g = 90.162(3)°
Volume	1898.0(6) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.414 Mg/m^3	
F(000)	838	
Theta range for data collection	2.16 to 28.36°	
Completeness to theta = 28.36°	89.1%	
Index ranges	-12<=h<=12, -17<=k<=16, -20<=l<=20	
Data collection scan type	phi and omega scans	
Reflections collected	18178	
Independent reflections	8454 [R_{int}= 0.0815]	
Absorption coefficient	0.467 mm^{-1}	
Absorption correction	None	
Structure Solution and Refinement		
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Difference Fourier map	
Structure refinement program	SHELXL-97 (Sheldrick, 1997)	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	8454 / 0 / 520	
Treatment of hydrogen atoms	Restrained	
Goodness-of-fit on F^2	1.776	
Final R indices [I>2s(I)]	R1 = 0.0525, wR2 = 0.0956	
R indices (all data)	R1 = 0.0663, wR2 = 0.0976	
Type of weighting scheme used	Sigma	
Weighting scheme used	$w=1/\sigma^2(Fo^2)$	
Max shift/error	0.000	
Average shift/error	0.000	
Largest diff. peak and hole	1.462 and -0.927 e.$Å^{-3}$	

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression

of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.
All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $Ph_2C(C_{13}H_8)(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2$. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Zr	6553(1)	3885(1)	2787(1)	11(1)
Cl(1)	7850(1)	5325(1)	3681(1)	18(1)
Cl(2)	6836(1)	4307(1)	1364(1)	18(1)
C(1)	4449(3)	3150(2)	3311(2)	12(1)
C(2)	4040(3)	3386(2)	2489(2)	12(1)
C(3)	3983(3)	4469(2)	2600(2)	12(1)
C(4)	4436(3)	4911(3)	3479(2)	15(1)
C(5)	4738(3)	4111(2)	3916(2)	13(1)
C(6)	6529(3)	2201(2)	3069(2)	11(1)
C(7)	7713(3)	2703(2)	3617(2)	14(1)
C(8)	8845(3)	2813(2)	3038(2)	15(1)
C(9)	8391(3)	2389(2)	2125(2)	14(1)
C(10)	6951(3)	2024(2)	2154(2)	14(1)
C(11)	7900(3)	3121(2)	4559(2)	14(1)
C(12)	9168(3)	3584(3)	4870(2)	18(1)
C(13)	10272(3)	3670(3)	4293(2)	19(1)
C(14)	10131(3)	3288(3)	3384(2)	17(1)
C(15)	6242(3)	1627(3)	1315(2)	16(1)
C(16)	6941(4)	1574(3)	531(2)	20(1)
C(17)	8369(3)	1890(3)	522(2)	21(1)
C(18)	9080(3)	2303(3)	1312(2)	18(1)
C(19)	3487(3)	4940(2)	1860(2)	14(1)
C(20)	1925(3)	4636(3)	1580(2)	16(1)
C(21)	1020(3)	6326(3)	2424(2)	21(1)
C(22)	2552(3)	6651(3)	2739(2)	21(1)
C(23)	3601(3)	6119(3)	2039(2)	16(1)
C(24)	3288(3)	6392(3)	1146(2)	18(1)
C(25)	1761(3)	6071(3)	825(2)	18(1)
C(26)	718(3)	6594(3)	1531(2)	21(1)
C(27)	1606(3)	4914(3)	693(2)	18(1)
C(28)	913(3)	5170(3)	2300(2)	19(1)
C(29)	5005(3)	2131(2)	3398(2)	12(1)
C(30)	4160(3)	1214(2)	2811(2)	15(1)
C(31)	2701(3)	1310(3)	2669(2)	18(1)
C(32)	1930(3)	480(3)	2192(2)	23(1)
C(33)	2573(4)	-449(3)	1867(2)	21(1)
C(34)	4010(4)	-545(3)	2013(2)	19(1)

C(35)	4791(3)	289(2)	2488(2)	16(1)
C(36)	4938(3)	1969(2)	4358(2)	14(1)
C(37)	3867(3)	2422(3)	4923(2)	19(1)
C(38)	3751(4)	2218(3)	5767(2)	25(1)
C(39)	4692(4)	1572(3)	6043(2)	25(1)
C(40)	5749(4)	1110(3)	5478(2)	19(1)
C(41)	5870(3)	1307(2)	4634(2)	15(1)
C(42)	6897(4)	7423(4)	1155(3)	40(1)
C(43)	7633(4)	8044(5)	1862(3)	55(2)
C(44)	8235(5)	8948(4)	1765(4)	48(1)
C(45)	8127(5)	9208(4)	989(4)	54(1)
C(46)	7385(5)	8592(4)	277(4)	50(1)
C(47)	6773(5)	7715(4)	364(3)	42(1)
C(48)	-278(5)	9278(4)	5476(3)	47(1)
C(49)	217(5)	8980(4)	4616(3)	48(1)
C(50)	503(5)	9700(4)	4142(3)	43(1)
H(2)	3834	2896	1944	15
H(4)	4528	5621	3741	18
H(5)	5077	4205	4517	16
H(11)	7161	3080	4962	20(9)
H(12)	9302	3856	5497	20(9)
H(13)	11133	3998	4535	11(8)
H(14)	10886	3343	2996	7(8)
H(15)	5285	1400	1299	16(9)
H(16)	6451	1317	-23	5(7)
H(17)	8837	1816	-33	18(9)
H(18)	10034	2530	1307	11(8)
H(19)	4083	4650	1327	1(7)
H(20)	1814	3882	1493	20(9)
H(21)	331	6678	2883	18(9)
H(22A)	2655	7399	2837	23(10)
H(22B)	2757	6471	3316	6(7)
H(23)	4587	6342	2247	21(9)
H(24A)	3968	6041	691	6(7)
H(24B)	3406	7137	1221	56(14)
H(25)	1554	6261	246	24(9)
H(26A)	-261	6379	1325	11(8)
H(26B)	789	7342	1612	21(9)
H(27A)	629	4696	484	25(10)
H(27B)	2274	4558	231	13(8)
H(28A)	1150	4992	2873	27(10)
H(28B)	-71	4938	2124	4(7)
H(31)	2245	1943	2900	26(10)
H(32)	944	550	2087	32(11)
H(33)	2031	-1017	1544	8(8)
H(34)	4463	-1181	1789	11(8)
H(35)	5778	218	2591	37(11)
H(37)	3217	2869	4737	29(10)
H(38)	3016	2526	6155	57(14)
H(39)	4614	1446	6623	25(10)
H(40)	6392	659	5665	50(13)
H(41)	6596	987	4244	19(9)
H(42)	6482	6802	1216	53(14)
H(43)	7728	7854	2417	51(13)

H(44)	8728	9381	2256	23(10)
H(45)	8560	9820	922	50(14)
H(46)	7305	8786	-277	59(15)
H(47)	6255	7299	-126	44(13)
H(48)	-465	8783	5807	64(15)
H(49)	362	8278	4348	82(19)
H(50)	856	9494	3551	73(17)

Table 3. Selected bond lengths [Å] and angles [°] for $Ph_2C(C_{13}H_8)(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2$.

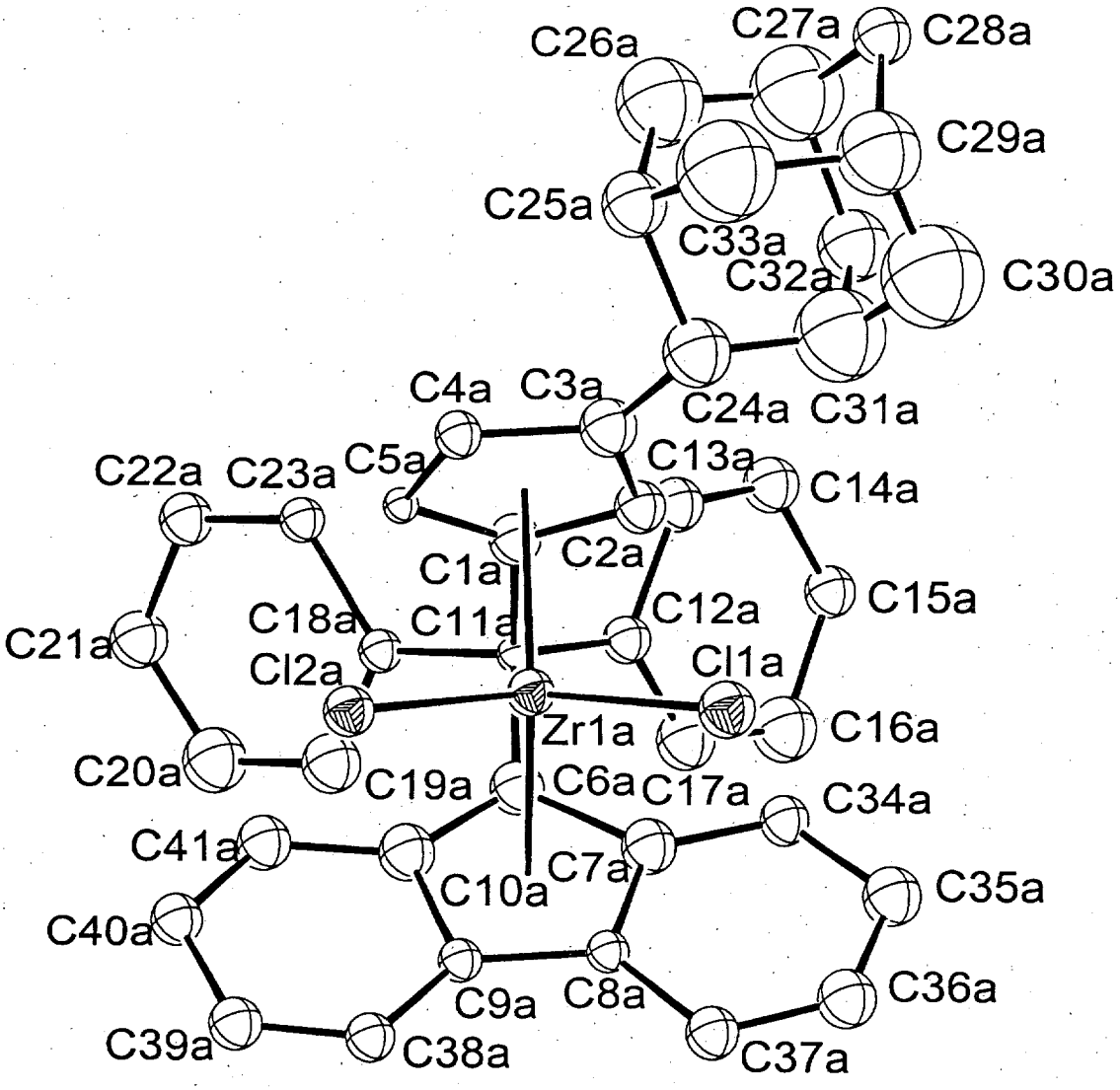
Zr-Pln(1)	2.1732(26)
Zr-Pln(2)	2.2362(30)
Zr-Cent(1)	2.1776(7)
Zr-Cent(2)	2.2486(7)
Zr-Cl(1)	2.4098(8)
Zr-Cl(2)	2.4062(9)
Zr-C(6)	2.416(3)
Zr-C(5)	2.424(3)
Zr-C(1)	2.448(3)
Zr-C(2)	2.466(3)
Zr-C(10)	2.499(3)
Zr-C(7)	2.514(3)
Zr-C(4)	2.532(3)
Zr-C(3)	2.583(3)
Zr-C(8)	2.678(3)
Zr-C(9)	2.684(3)
Pln(1)-Zr-Pln(2)	108.18(25)
Cent(1)-Zr-Cent(2)	118.02(3)
Cl(2)-Zr-Cl(1)	96.83(3)
C(1)-C(29)-C(6)	99.6(2)

Pln(1) is the plane defined by C1, C2, C3, C4 and C5.
Pln(2) is the plane defined by C6, C7, C8, C9 and C10.
Cent(1) is the centroid of C1, C2, C3, C4 and C5.
Cent(2) is the centroid of C6, C7, C8, C9 and C10.

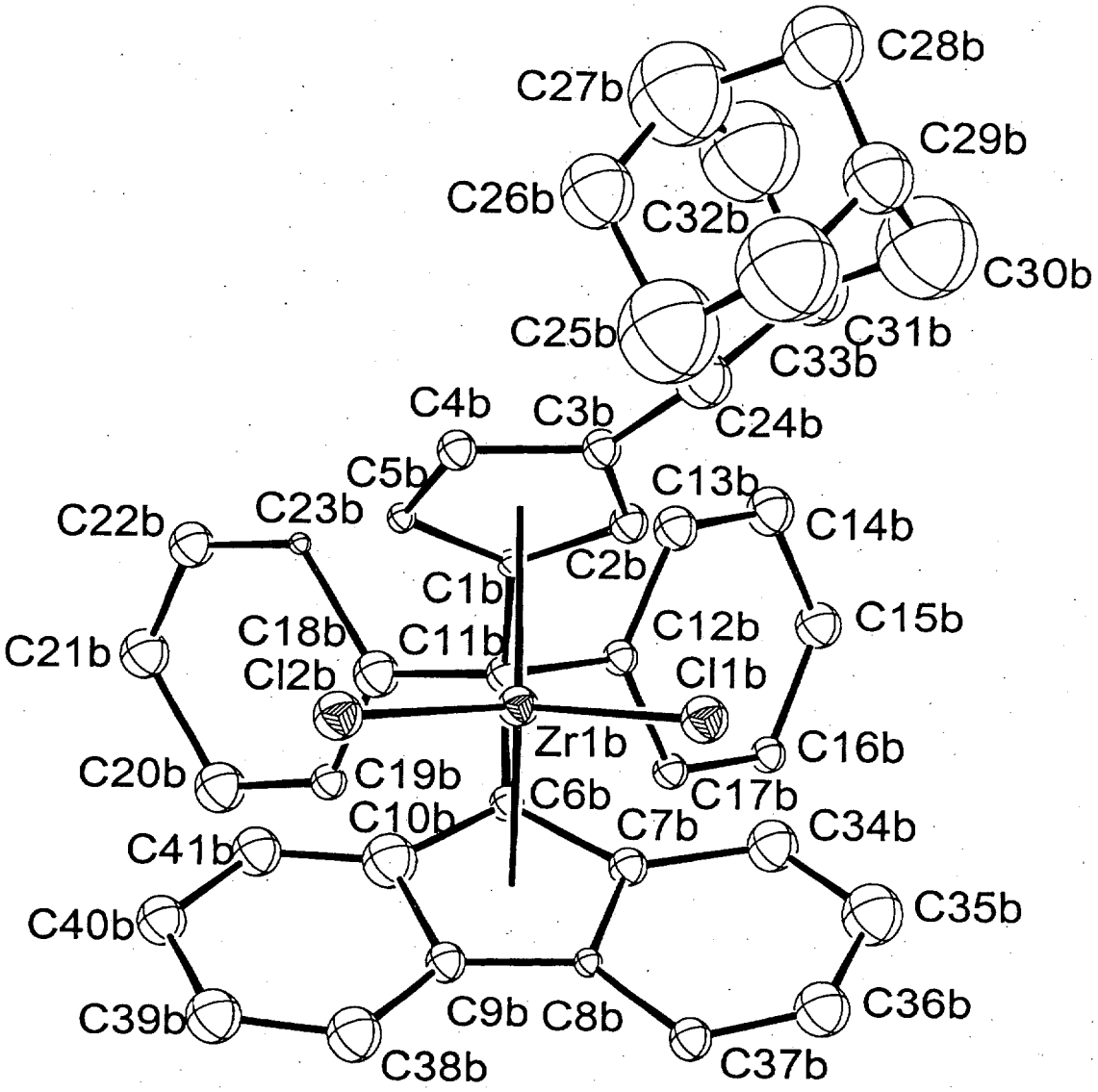
X-ray Crystal Structure Data for

$Ph_2C(C_{13}H_8)(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2 \cdot (C_6H_6)_2$

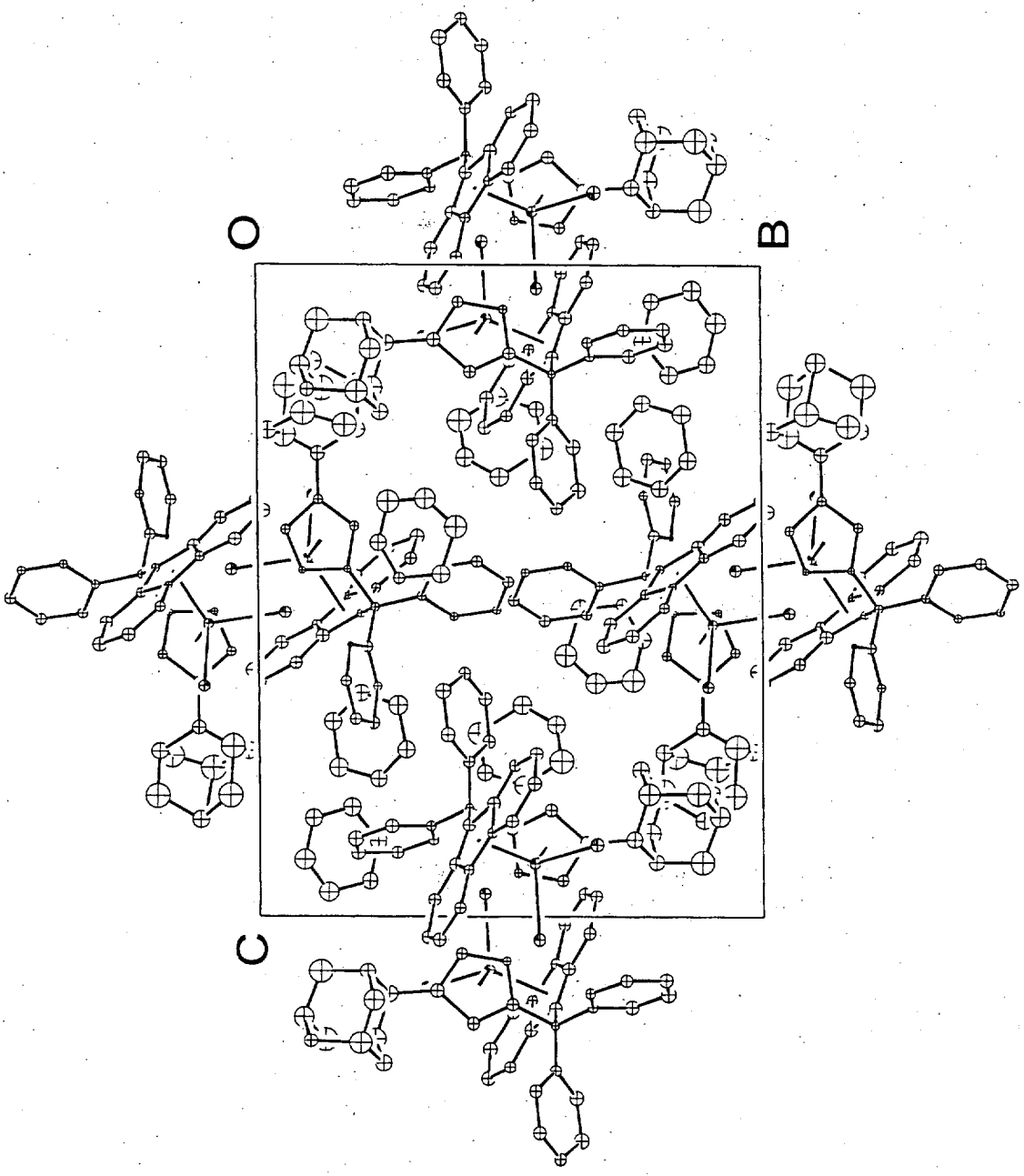
Cambridge Database (CCDC) 137247



Labeled view of molecule A with 50% probability ellipsoids



Labeled view of molecule B with 50% probability ellipsoids



Depiction of unit cell contents showing the unit cell boundaries

Table 1. Crystal Data and Structure Refinement for $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$.

Empirical formula	$C_{53}H_{48}Cl_2Zr$ $[C_{41}H_{36}Cl_2Zr \cdot 2(C_6H_6)]$	
Formula weight	847.09 [690.87 · 2(78.11)]	
Crystallization solvent	benzene	
Crystal habit	blade	
Crystal size	0.48 x 0.09 x 0.04 mm^3	
Crystal color	bright red	
Data Collection		
Preliminary photograph(s)	rotation	
Type of diffractometer	CAD4	
Wavelength	0.71073 Å MoKa	
Data collection temperature	84 K	
Theta range for 25 reflections used in lattice determination	11 to 14°	
Unit cell dimensions	a = 13.242(6) Å	a= 82.67(3)°
	b = 17.098(10) Å	b= 73.29(3)°
	c = 21.311(5) Å	g = 67.26(5)°
Volume	4261(3) $Å^3$	
Z	4	
Crystal system	Triclinic	
Space group	$P\bar{1}$ (#2)	
Density (calculated)	1.320 g/cm^3	
F(000)	1760	
Theta range for data collection	1.5 to 20°	
Completeness to theta = 20.00°	100.0 %	
Index ranges	-12<=h<=12, -16<=k<=16, -20<=l<=20	
Data collection scan type	ω–scan	
Reflections collected	17254	
Independent reflections	7934 [R_{int}= 0.0897; GOF_{merge}= 1.01]	
Absorption coefficient	0.419 mm^{-1}	
Absorption correction	ψ–scan (North, Phillips & Matthews, 1968)	
Max. and min. transmission	1.29 and 0.60	
Number of standards	3 reflections measured every 75 min	
Variation of standards	0.41%	
Structure Solution and Refinement		
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Primary solution method	direct methods	
Secondary solution method	difference map	
Hydrogen placement	geometric	
Structure refinement program	SHELXL-97 (Sheldrick, 1997)	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	7934 / 0 / 449	
Treatment of hydrogen atoms	no refinement	
Goodness-of-fit on F^2	2.909	
Final R indices [I>2s(I)]	R1 = 0.1567, wR2 = 0.2781	
R indices (all data)	R1 = 0.2372, wR2 = 0.2922	
Type of weighting scheme used	calculated	
Weighting scheme used	$w=1/\sigma^2(F_o^2)$	
Max shift/error	0.005	
Average shift/error	0.000	

Largest diff. peak and hole 3.985 and -3.956 e.Å^{-3}

Special Details

A tiny bright red blade was mounted on a glass fiber with Paratone-N oil. Data were collected with 1.4° ω-scans. The individual backgrounds were replaced by a background function of 2θ derived from those reflections with I < 3σ(I); a number of high backgrounds were removed from this calculation. The GOF_merge was 1.01 (7932 multiples) in point group $\bar{1}$; R_merge was 0.069 for 5527 duplicates with F_o > 0. Ψ–scan data were used for the absorption correction. One outlier reflection (0 1 1) was omitted from the refinement.

Weights w are calculated as $1/\sigma^2(F_o^2)$; variances ($\sigma^2(F_o^2)$) were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014<I>)^2$. The refinement of F^2 is as always against all reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement.

The asymmetric unit consists of two molecules, with different orientations of the adamantyl group, and four molecules of benzene. Overlaps of the two molecules with each other and with the structure obtained from a different solvate are provided. Since the crystal was small and the unit cell large, a 2θ limit of 40° was used in collecting data. The background is anisotropic and, as a result, reflections with small values of h were apparently truncated. Coupled with the lack of high angle data, this systematic error caused most atoms to go non-positive definite during refinement. Consequently all heavy atoms were refined isotropically; no hydrogen atom parameters were refined. Not surprisingly, the largest excursions in the final difference map are big (~4 e.Å^{-3}) and near the two Zr atoms. Nonetheless, this structure adequately shows the conformations of the two molecules.

This crystal was obtained from the same vial and had the same habit as $Ph_2C(C_{13}H_8)(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2 \cdot (C_6H_6)_{1.5}$, which was examined months later. It is interesting to speculate that the structure of $Ph_2C(C_{13}H_8)(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2 \cdot (C_6H_6)_{1.5}$ may have resulted from the slow loss of benzene from $Ph_2C(C_{13}H_8)(3\text{-}(2\text{-adamantyl})\text{-}C_5H_3)ZrCl_2 \cdot (C_6H_6)_2$ accompanied by rearrangement of the molecules.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Zr1A	2375(2)	4540(2)	816(1)	21(1)
Cl1A	3856(6)	3298(4)	1108(3)	31(2)
Cl2A	3143(6)	4458(4)	-359(3)	25(2)
C1A	330(20)	4997(16)	1352(11)	25(7)
C2A	860(20)	4216(16)	1637(11)	26(7)
C3A	1260(20)	3503(17)	1140(11)	32(7)
C4A	1010(20)	3986(15)	562(10)	21(7)
C5A	480(19)	4884(14)	672(9)	12(6)
C6A	1340(20)	5854(16)	1413(11)	28(7)
C7A	2270(20)	5358(17)	1734(11)	29(7)
C8A	3290(20)	5390(15)	1289(10)	18(6)
C9A	3060(20)	5865(15)	713(10)	19(6)
C10A	1830(20)	6121(17)	799(11)	30(7)

C11A	130(20)	5846(14)	1669(10)	10(6)
C12A	-310(20)	5851(16)	2374(11)	22(7)
C13A	-1090(20)	5450(16)	2688(11)	27(7)
C14A	-1630(20)	5521(16)	3339(11)	30(7)
C15A	-1410(20)	5930(15)	3736(11)	24(7)
C16A	-650(20)	6356(17)	3462(12)	40(8)
C17A	-160(20)	6265(16)	2791(11)	33(7)
C18A	-680(20)	6605(15)	1396(10)	18(6)
C19A	-680(20)	7390(17)	1394(11)	33(7)
C20A	-1470(20)	8108(18)	1196(11)	39(8)
C21A	-2320(20)	8065(17)	979(11)	32(7)
C22A	-2390(20)	7281(15)	986(10)	26(7)
C23A	-1610(20)	6556(16)	1182(9)	18(6)
C24A	1750(30)	2551(18)	1188(12)	44(8)
C25A	1200(20)	2112(18)	836(13)	41(8)
C26A	20(30)	2230(20)	1285(14)	75(11)
C27A	-30(40)	1960(20)	1937(17)	86(12)
C28A	680(20)	984(16)	1906(11)	31(7)
C29A	1970(30)	850(20)	1546(14)	68(11)
C30A	2320(40)	1280(30)	1888(18)	100(14)
C31A	1650(30)	2260(20)	1877(16)	82(12)
C32A	550(30)	2420(19)	2255(13)	49(9)
C33A	2020(30)	1200(20)	838(16)	97(14)
C34A	2290(20)	4939(15)	2317(10)	23(7)
C35A	3340(20)	4507(17)	2500(12)	32(7)
C36A	4350(20)	4548(17)	2040(11)	34(7)
C37A	4350(20)	4999(15)	1471(11)	27(7)
C38A	3750(20)	6041(15)	130(10)	23(7)
C39A	3370(20)	6451(16)	-359(11)	27(7)
C40A	2200(20)	6685(16)	-322(11)	25(7)
C41A	1480(20)	6543(15)	261(10)	27(7)
H2A	948	4138	2060	31
H4A	1166	3744	161	25
H5A	277	5309	362	14
H13A	-1242	5122	2437	33
H14A	-2165	5273	3509	36
H15A	-1741	5938	4184	29
H16A	-493	6677	3714	48
H17A	354	6537	2615	40
H19A	-109	7454	1534	40
H20A	-1418	8633	1212	47
H21A	-2836	8547	831	39
H22A	-2977	7238	855	32
H23A	-1677	6034	1179	22
H24A	2562	2367	965	53
H25A	1181	2339	392	50
H26A	-451	2832	1282	89
H26B	-314	1932	1102	89
H27A	-812	2076	2191	103
H28A	393	709	1666	38
H28B	625	738	2345	38
H29A	2435	245	1541	81
H30A	3121	1162	1699	120
H30B	2219	1072	2338	120

H31A	2004	2532	2078	98
H32A	126	3026	2271	59
H32B	558	2207	2698	59
H33A	2785	1162	618	117
H33B	1822	852	600	117
H34A	1615	4930	2604	28
H35A	3363	4215	2898	39
H36A	5046	4248	2139	40
H37A	5016	5057	1205	33
H38A	4527	5856	89	28
H39A	3850	6589	-729	33
H40A	1920	6929	-682	30
H41A	711	6751	289	33
Zr1B	2710(2)	9015(2)	5509(1)	16(1)
Cl1B	1250(6)	8919(4)	6468(3)	23(2)
Cl2B	1810(6)	10527(4)	5325(3)	24(2)
C1B	4771(19)	8241(14)	5337(9)	8(6)
C2B	4257(19)	8099(15)	5998(9)	14(6)
C3B	3810(20)	8809(15)	6395(10)	15(6)
C4B	4000(20)	9456(15)	5945(9)	15(6)
C5B	4566(18)	9134(13)	5316(9)	8(6)
C6B	3840(20)	7975(14)	4661(9)	12(6)
C7B	2940(20)	7681(14)	5043(10)	15(6)
C8B	1878(19)	8230(14)	4928(9)	8(6)
C9B	2090(20)	8853(15)	4479(10)	16(6)
C10B	3310(20)	8739(17)	4312(11)	29(7)
C11B	5030(20)	7702(15)	4762(10)	13(6)
C12B	5600(20)	6770(14)	4924(9)	12(6)
C13B	6290(20)	6508(15)	5358(10)	18(6)
C14B	6900(20)	5672(15)	5454(10)	22(7)
C15B	6800(20)	5054(16)	5138(10)	21(6)
C16B	6117(19)	5284(14)	4715(9)	12(6)
C17B	5517(19)	6134(14)	4612(9)	12(6)
C18B	5830(20)	7864(15)	4138(10)	21(7)
C19B	5910(20)	7663(14)	3535(9)	13(6)
C20B	6640(20)	7745(16)	2967(11)	25(7)
C21B	7470(20)	8099(15)	3028(11)	23(7)
C22B	7430(20)	8281(15)	3619(10)	20(6)
C23B	6693(18)	8196(13)	4173(9)	5(5)
C24B	3360(20)	8815(17)	7111(11)	32(7)
C25B	2900(40)	9490(30)	7390(18)	103(15)
C26B	3800(30)	9800(20)	7454(14)	54(9)
C27B	4750(40)	9100(30)	7728(18)	107(15)
C28B	4130(30)	8920(20)	8521(14)	66(10)
C29B	3050(30)	8836(19)	8513(14)	49(9)
C30B	3560(40)	7990(20)	8161(17)	101(14)
C31B	4170(30)	8037(19)	7471(12)	47(9)
C32B	5100(40)	8280(30)	7541(18)	99(14)
C33B	2360(40)	9430(30)	8148(17)	105(15)
C34B	2950(20)	6983(16)	5501(10)	25(7)
C35B	1940(20)	6851(17)	5842(12)	36(8)
C36B	930(20)	7423(16)	5685(11)	31(7)
C37B	860(20)	8058(15)	5245(9)	18(6)

C38B	1360(20)	9550(16)	4205(10)	30(7)
C39B	1750(20)	10113(17)	3777(11)	31(7)
C40B	2940(20)	9970(16)	3609(10)	23(7)
C41B	3630(20)	9268(15)	3888(10)	23(7)
H2B	4217	7576	6157	17
H4B	3775	10019	6053	18
H5B	4776	9444	4945	10
H13B	6338	6915	5588	22
H14B	7378	5517	5731	27
H15B	7198	4483	5212	25
H16B	6057	4871	4499	14
H17B	5049	6285	4329	14
H19B	5396	7434	3504	15
H20B	6623	7592	2567	30
H21B	7999	8189	2660	28
H22B	7969	8488	3652	24
H23B	6718	8342	4573	5
H24B	2719	8639	7161	38
H25B	2355	9907	7170	124
H26C	3440	10277	7744	64
H26D	4140	9988	7028	64
H27B	5391	9268	7691	129
H28C	4613	8401	8693	79
H28D	3972	9387	8792	79
H29B	2599	8783	8960	59
H30C	4085	7574	8390	122
H30D	2962	7784	8184	122
H31B	4452	7498	7246	56
H32C	5458	7904	7862	119
H32D	5674	8200	7125	119
H33C	2129	9985	8329	126
H33D	1685	9307	8212	126
H34B	3638	6611	5574	30
H35B	1939	6415	6151	44
H36B	261	7348	5909	37
H37B	179	8382	5146	21
H38B	593	9637	4313	35
H39B	1248	10575	3601	37
H40B	3228	10335	3324	28
H41B	4405	9168	3760	28
C1	860(30)	8430(20)	2283(14)	60(10)
C2	1800(30)	7650(19)	2112(13)	48(9)
C3	2240(30)	7090(20)	2564(13)	53(9)
C4	1790(30)	7260(20)	3240(14)	63(10)
C5	860(30)	7989(19)	3427(14)	48(9)
C6	430(30)	8550(20)	2987(13)	53(9)
C7	4540(30)	7660(20)	1163(13)	50(9)
C8	4400(30)	8180(20)	1678(14)	53(9)
C9	4500(30)	8940(20)	1514(13)	49(9)
C10	4770(30)	9120(20)	874(15)	74(11)
C11	4940(30)	8640(20)	383(15)	66(10)
C12	4830(20)	7834(19)	549(13)	42(8)
C13	6240(20)	5533(19)	2207(13)	44(8)

C14	7020(30)	4760(20)	2014(15)	64(10)
C15	7100(40)	4000(30)	2388(18)	101(14)
C16	6500(30)	4110(20)	2945(14)	55(9)
C17	5610(30)	4790(20)	3245(14)	60(10)
C18	5510(30)	5660(20)	2812(15)	76(11)
C19	1280(20)	2783(15)	4803(11)	23(7)
C20	620(30)	3620(20)	4741(13)	55(9)
C21	800(30)	3910(30)	4011(16)	84(12)
C22	1510(30)	3310(20)	3589(17)	76(11)
C23	2040(30)	2570(30)	3631(18)	89(13)
C24	1930(30)	2370(20)	4255(13)	49(9)
H1	553	8825	1978	72
H2	2127	7519	1671	58
H3	2856	6596	2426	63
H4	2105	6881	3549	76
H5	520	8096	3871	57
H6	-179	9040	3140	64
H7	4418	7160	1281	59
H8	4237	7998	2114	64
H9	4394	9310	1829	59
H10	4852	9639	761	88
H11	5128	8825	-51	79
H12	4960	7457	231	51
H13	6206	5991	1916	52
H14	7528	4718	1605	77
H15	7584	3469	2222	121
H16	6668	3628	3216	65
H17	5120	4763	3652	73
H18	5010	6195	2966	91
H19	1268	2514	5212	28
H20	135	3966	5091	66
H21	435	4467	3881	101
H22	1636	3517	3159	91
H23	2449	2198	3284	107
H24	2405	1826	4330	59

Table 3. Selected bond lengths [Å] and angles [°] for $Ph_2C(3\text{-}(2\text{-adamantyl})C_5H_3)(C_{13}H_8)ZrCl_2$.

Zr1A-Cp1A	2.183
Zr1A-Cp2A	2.248
Zr1A-Pl1A	2.177(13)
Zr1A-Pl2A	2.226(12)
Zr1A-Cl2A	2.416(6)
Zr1A-Cl1A	2.428(7)
Zr1A-C6A	2.43(2)
Zr1A-C5A	2.45(2)
Zr1A-C2A	2.45(3)

Zr1A-C1A	2.46(3)
Zr1A-C7A	2.49(2)
Zr1A-C10A	2.51(3)
Zr1A-C4A	2.55(3)
Zr1A-C3A	2.63(3)
Zr1A-C8A	2.66(3)
Zr1A-C9A	2.71(3)
Zr1B-Cp1B	2.202
Zr1B-Cp2B	2.248
Zr1B-Pl1B	2.196(11)
Zr1B-Pl2B	2.200(19)
Zr1B-Cl1B	2.414(7)
Zr1B-Cl2B	2.427(7)
Zr1B-C6B	2.42(2)
Zr1B-C5B	2.46(2)
Zr1B-C2B	2.46(2)
Zr1B-C1B	2.47(2)
Zr1B-C7B	2.48(2)
Zr1B-C10B	2.49(2)
Zr1B-C4B	2.54(2)
Zr1B-C3B	2.61(2)
Zr1B-C8B	2.63(2)
Zr1B-C9B	2.63(2)
Cp1A-Zr1A-Cp2A	117.9
Cp1A-Zr1A-Cl1A	109.7
Cp1A-Zr1A-Cl2A	108.9
Cp2A-Zr1A-Cl1A	110.2
Cp2A-Zr1A-Cl2A	110.7
Cl2A-Zr1A-Cl1A	97.5(2)
Pl1A-Pl2A	74(1)
C6A-C11A-C1A	99.1(18
Cp1B-Zr1B-Cp2B	117.8
Cp1B-Zr1B-Cl1B	109.0
Cp1B-Zr1B-Cl2B	110.0
Cp2B-Zr1B-Cl1B	111.6
Cp2B-Zr1B-Cl2B	110.5
Cl1B-Zr1B-Cl2B	95.6(2)
Pl1B-Pl2B	73(1)
C1B-C11B-C6B	100.3(17)

Cp1A is the centroid formed by C1A, C2A, C3A, C4A, C5A
Cp2A is the centroid formed by C6A, C7A, C8A, C9A, C10A
Pl1A is the plane formed by C1A, C2A, C3A, C4A, C5A
Pl2A is the plane formed by C6A, C7A, C8A, C9A, C10A
Cp1B is the centroid formed by C1B, C2B, C3B, C4B, C5B
Cp2B is the centroid formed by C6B, C7B, C8B, C9B, C10B
Pl1B is the plane formed by C1B, C2B, C3B, C4B, C5B
Pl2B is the plane formed by C6B, C7B, C8B, C9B, C10B

Exxon used the following protocol for mechanical testing:

Plaques suitable for physical property testing were compression molded on a Carver hydraulic press. 6.5g of polymer was molded between brass plates (0.05" thick) lined with Teflon coated aluminum foil. A 0.033" thick chase with a square opening 4" x 4" was used to control sample thickness. After one minute of preheat at 120, under minimal pressure, the hydraulic load was gradually increased to ~10,000 - 15,000 lbs. at which it was held for three minutes. Subsequently the sample and molding plates were cooled for three minutes under ~10,000 to 15,000 lbs. load between the water cooled platens of the press. Plaques were allowed to equilibrate at room temperature for a minimum of one week prior to physical property testing. Dogbones for tensile testing were cut from compression molded plaques using a mallet handle die. Specimen dimensions were those specified in ASTM D 1708. Tensile properties were measured on an Instron model 4502 equipped with a 22.48 lb. load cell and pneumatic jaws fitted with serrated grip faces. Five specimens of each sample were tested. Deformation was performed at a constant crosshead speed of 5.0 in./min. with a data sampling rate of 25 points/second. Jaw separation prior to testing was 0.876", from which strains were calculated assuming affine deformation. Initial modulus, stress and strain at yield (where evident), stress at 100%, 200%, 300%, 400%, 500% and 1,000% strain, and stress and strain at break were calculated. A minimum of five specimens from each plaque were tested, the results being reported as the average value. All stresses quoted are "engineering" values, *i.e.*, they are calculated based upon the original cross-sectional area of the specimen, taking no account of reduced cross-section as a function of increasing strain. Strain values in excess of 500% are questionable; most samples pulled out of the grips to some extent at higher strains. Thus, the strain calculated from crosshead separation is larger than the strain experienced in the gauge region of the sample. This phenomenon was particularly apparent in samples that exhibited high

degrees of strain hardening. Elastic recovery experiments were performed on the Instron 4502 tensile tester using samples with the same specimen dimensions as those used in tensile experiments. Three specimens of each sample were tested. Prior to testing a pair of fiducial ink marks were placed on the gauge region of the sample 0.5" apart (with an Ultra Fine Point Sharpie marker pen). The sample was extended to a nominal 200% elongation (crosshead displacement 1.752") at a crosshead speed of 20 in./min. Once it reached this extension, the crosshead travel was automatically reversed and the crosshead returned to its original position at 20 in./min. The sample was immediately removed from the grips and the separation of the ink marks was measured with calipers. Recovery from the fiducial marks is calculated according to: Recovery from 200% strain (%) = 100 (E - 0.5)/(0.5), where E = Fiducial mark separation after 24 hours. Results: All samples drew affinely. No samples exhibited a yield peak. All samples strain whitened to some extent. This was particularly noticeable in the sample from Entry 15, in which the whitening was irreversible.

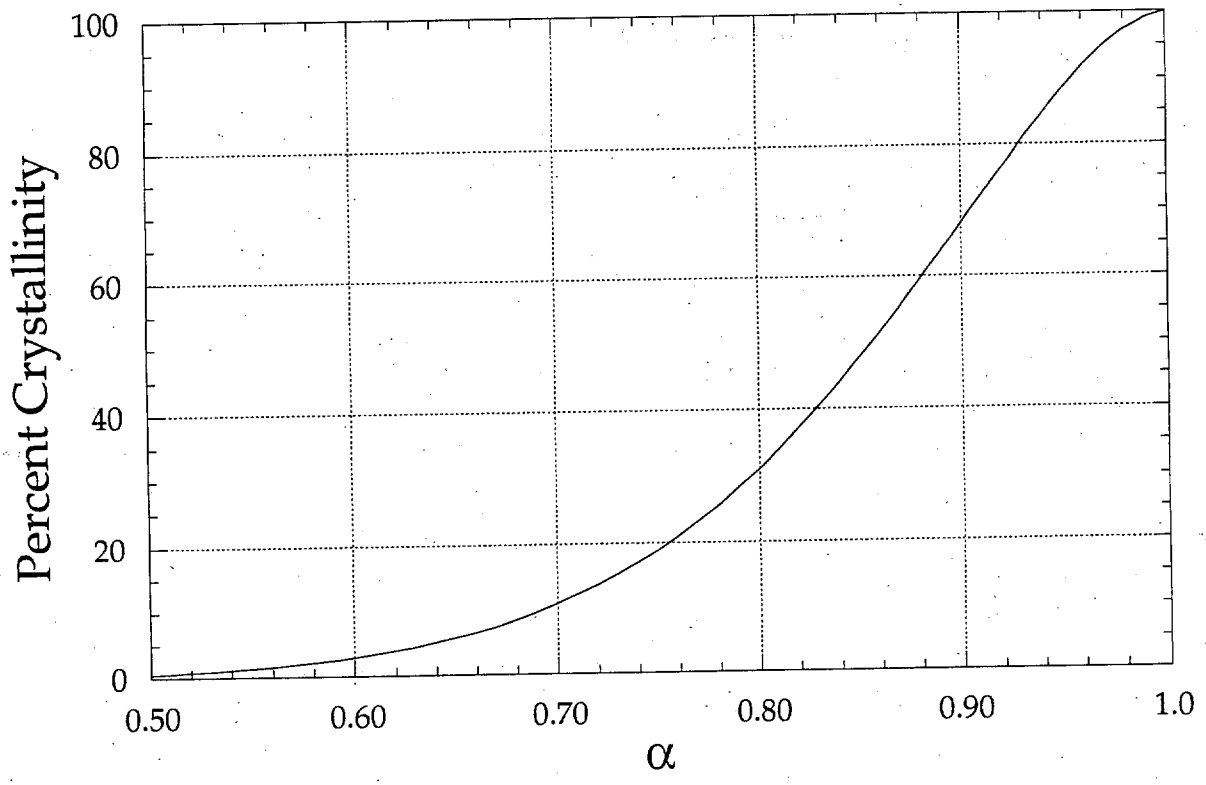
Calculated isotactic block length distributions:

Entry	1	3	4	5	8	9
M_n =	44,200	43,000	18,700	43,000(est.)	273,000	204,000
α =	0.504	0.623	0.627	0.610	0.578	0.557
n	N_n	N_n	N_n	N_n	N_n	N_n
1	389.70	265.24	113.79	276.98	1946.57	1549.51
3	65.12	45.24	19.38	47.40	333.89	264.96
5	32.82	28.19	12.15	28.92	192.99	147.59
7	16.54	17.56	7.62	17.64	111.55	82.20
9	8.34	10.94	4.78	10.76	64.48	45.79
11	4.20	6.82	3.00	6.56	37.27	25.50
13	2.12	4.25	1.88	4.00	21.54	14.21
15	1.07	2.65	1.18	2.44	12.45	7.91
17	0.54	1.65	0.74	1.49	7.20	4.41
19	0.27	1.03	0.46	0.91	4.16	2.45
21	0.14	0.64	0.29	0.55	2.40	1.37
23	0.07	0.40	0.18	0.34	1.39	0.76
25	0.03	0.25	0.11	0.21	0.80	0.42
27	0.02	0.15	0.07	0.13	0.46	0.24
29	0.01	0.10	0.04	0.08	0.27	0.13
31	0.00	0.06	0.03	0.05	0.16	0.07
33	0.00	0.04	0.02	0.03	0.09	0.04
35	0.00	0.02	0.01	0.02	0.05	0.02
37	0.00	0.01	0.01	0.01	0.03	0.01
39	0.00	0.01	0.00	0.01	0.02	0.01
41	0.00	0.01	0.00	0.00	0.01	0.00
43	0.00	0.00	0.00	0.00	0.01	0.00
45	0.00	0.00	0.00	0.00	0.00	0.00
47	0.00	0.00	0.00	0.00	0.00	0.00
49	0.00	0.00	0.00	0.00	0.00	0.00
51	0.00	0.00	0.00	0.00	0.00	0.00
53	0.00	0.00	0.00	0.00	0.00	0.00
55	0.00	0.00	0.00	0.00	0.00	0.00
57	0.00	0.00	0.00	0.00	0.00	0.00
59	0.00	0.00	0.00	0.00	0.00	0.00
61	0.00	0.00	0.00	0.00	0.00	0.00
63	0.00	0.00	0.00	0.00	0.00	0.00
65	0.00	0.00	0.00	0.00	0.00	0.00
$\Sigma(N_n) \mid n \geq 21$	0.28	1.70	0.78	1.42	5.70	3.09
calc. % cryst.	0.60	4.04	4.27	3.36	2.08	1.50

Entry	10	11	12	15	16	18
M_n =	463,000	416,000	330,000	417,000	54,400	224,000
α =	0.579	0.587	0.588	0.576	0.576	0.438
n	N_n	N_n	N_n	N_n	N_n	N_n
1	3291.18	2884.56	2281.08	2991.62	390.27	2336.47
3	564.57	494.91	391.36	513.08	66.93	368.20
5	326.89	290.51	230.12	295.53	38.55	161.27
7	189.27	170.53	135.31	170.23	22.21	70.64
9	109.59	100.10	79.56	98.05	12.79	30.94
11	63.45	58.76	46.78	56.48	7.37	13.55
13	36.74	34.49	27.51	32.53	4.24	5.94
15	21.27	20.25	16.17	18.74	2.44	2.60
17	12.32	11.88	9.51	10.79	1.41	1.14
19	7.13	6.98	5.59	6.22	0.81	0.50
21	4.13	4.10	3.29	3.58	0.47	0.22
23	2.39	2.40	1.93	2.06	0.27	0.10
25	1.38	1.41	1.14	1.19	0.15	0.04
27	0.80	0.83	0.67	0.68	0.09	0.02
29	0.46	0.49	0.39	0.39	0.05	0.01
31	0.27	0.29	0.23	0.23	0.03	0.00
33	0.16	0.17	0.14	0.13	0.02	0.00
35	0.09	0.10	0.08	0.08	0.01	0.00
37	0.05	0.06	0.05	0.04	0.01	0.00
39	0.03	0.03	0.03	0.02	0.00	0.00
41	0.02	0.02	0.02	0.01	0.00	0.00
43	0.01	0.01	0.01	0.01	0.00	0.00
45	0.01	0.01	0.01	0.00	0.00	0.00
47	0.00	0.00	0.00	0.00	0.00	0.00
49	0.00	0.00	0.00	0.00	0.00	0.00
51	0.00	0.00	0.00	0.00	0.00	0.00
53	0.00	0.00	0.00	0.00	0.00	0.00
55	0.00	0.00	0.00	0.00	0.00	0.00
57	0.00	0.00	0.00	0.00	0.00	0.00
59	0.00	0.00	0.00	0.00	0.00	0.00
61	0.00	0.00	0.00	0.00	0.00	0.00
63	0.00	0.00	0.00	0.00	0.00	0.00
65	0.00	0.00	0.00	0.00	0.00	0.00
$\Sigma(N_n) \mid n \geq 21$	9.81	9.92	7.98	8.45	1.10	0.39
calc. % cryst.	2.12	2.39	2.43	2.02	2.02	0.16

Entry	19	20	22	23	24
M_n =	168,000	38,500	349,000	172,000	242,000
α =	0.506	0.753	0.575	0.610	0.630
n	N_n	N_n	N_n	N_n	N_n
1	1473.27	140.90	2511.44	1107.90	1457.58
3	246.49	21.02	430.69	189.62	248.00
5	124.73	15.82	247.65	115.67	156.24
7	63.11	11.92	142.40	70.56	98.43
9	31.93	8.97	81.88	43.04	62.01
11	16.16	6.76	47.08	26.25	39.07
13	8.18	5.09	27.07	16.02	24.61
15	4.14	3.83	15.57	9.77	15.51
17	2.09	2.88	8.95	5.96	9.77
19	1.06	2.17	5.15	3.64	6.15
21	0.54	1.64	2.96	2.22	3.88
23	0.27	1.23	1.70	1.35	2.44
25	0.14	0.93	0.98	0.83	1.54
27	0.07	0.70	0.56	0.50	0.97
29	0.04	0.53	0.32	0.31	0.61
31	0.02	0.40	0.19	0.19	0.38
33	0.01	0.30	0.11	0.11	0.24
35	0.00	0.22	0.06	0.07	0.15
37	0.00	0.17	0.04	0.04	0.10
39	0.00	0.13	0.02	0.03	0.06
41	0.00	0.10	0.01	0.02	0.04
43	0.00	0.07	0.01	0.01	0.02
45	0.00	0.05	0.00	0.01	0.02
47	0.00	0.04	0.00	0.00	0.01
49	0.00	0.03	0.00	0.00	0.01
51	0.00	0.02	0.00	0.00	0.00
53	0.00	0.02	0.00	0.00	0.00
55	0.00	0.01	0.00	0.00	0.00
57	0.00	0.01	0.00	0.00	0.00
59	0.00	0.01	0.00	0.00	0.00
61	0.00	0.01	0.00	0.00	0.00
63	0.00	0.00	0.00	0.00	0.00
65	0.00	0.00	0.00	0.00	0.00
$\Sigma(N_n) \mid n \geq 21$	1.09	6.62	6.96	5.69	10.48
calc. % cryst.	0.63	19.61	1.99	3.36	4.45

A reasonable assumption was advanced that crystallites are made of isotactic sequences 21 propylene units or longer. With this assumption it is possible to estimate the percent crystallinity of a polymer sample based solely on the parameter α. Since this estimation is a percentage, the estimation is independent of molecular weight, although, in practice, the estimation is valid for DP >> 21. The Figure below shows the calculated percent crystallinity (percent of the monomers in isotactic blocks with n ≥ 21) as a function of α. The data points that make up the plot are also provided.



α	% cryst.	α	% cryst.
0.50	0.5615	0.76	21.087
0.51	0.6731	0.77	23.335
0.52	0.8037	0.78	25.758
0.53	0.9557	0.79	28.357
0.54	1.1322	0.80	31.139
0.55	1.3361	0.81	34.102
0.56	1.5711	0.82	37.248
0.57	1.8409	0.83	40.574
0.58	2.1497	0.84	44.075
0.59	2.5019	0.85	47.742
0.60	2.9024	0.86	51.563
0.61	3.3563	0.87	55.523
0.62	3.8692	0.88	59.599
0.63	4.4470	0.89	63.767
0.64	5.0959	0.90	67.992
0.65	5.8226	0.91	72.237
0.66	6.6341	0.92	76.452
0.67	7.5374	0.93	80.583
0.68	8.5402	0.94	84.563
0.69	9.6502	0.95	88.314
0.70	10.875	0.96	91.747
0.71	12.223	0.97	94.759
0.72	13.703	0.98	97.232
0.73	15.321	0.99	99.030
0.74	17.086	1.00	100.00
0.75	19.006		